NANOSTRUCTURED METAL OXIDES FOR HIGH POWER BATTERIES

Interim Report

JPL Task 1012

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A. OBJECTIVES

Lithium ion rechargeable batteries are the next-generation rechargeable battery systems for NASA's future needs. Despite their distinct advantages in specific energy, operating temperature range and self-discharge, they have relatively lower power densities than the alkaline nickel systems, attributed mainly to the slow lithium intercalation processes at the electrode. Electrodes with nanostructured features, e.g., Nanofibers, are expected to have much larger effective surface and interfacial areas, and thus higher power densities. The objectives of the proposed work are to synthesize nanostructured metal oxides for cathode applications in lithium rechargeable batteries, using novel template and sol-gel or electrolytic synthetic techniques. Such nanostructured morphologies will enhance the power densities and energy densities of the micropower sources by 1-2 orders of magnitude, compared to the state-of-art devices, while preserving comparable footprints. These nanocathodes will benefit, apart from the batteries, several other electrochemical devices, e.g., electrochromic devices and microsensors.

B. PROGRESS AND RESULTS

High surface electrodes, e.g., nanowires with high aspect ratios, are possible cathode morphologies for high power density applications, as demonstrated with vanadium oxide cathodes.[1] These cathodes were fabricated by sol-gel deposition into nano-channels in porous alumina templates.[2] The procedure adopted by us to get nanowires of transition metal oxides is described below.

We used alumina templates, synthesized in-house with a typical diameter of 20 nm (Fig.1). The porosity and pore diameter of the alumina templates can, however, be varied by changing the anodizing conditions of the aluminum sheet. This in-house capability allows for direct on-silicon fabrication, of interest for micro-power applications. A current collector, either Au or Pt, is deposited on one end of the porous alumina and from the open end, transition metals, either cobalt or nickel, are deposited electrochemically. The template is then digested, leaving nanowires of either cobalt or nickel, as illustrated in Fig. 2. Preliminary attempts to lithiate these nanometallic wires, to form lithium cobalt or nickel oxide nanowires, haven't been successful. Further work is underway to refine the nanostructure and obtain the nanowires in the desired oxidation state. Meanwhile, using a similar approach, we have been able to successfully fabricate freestanding arrays of manganese oxide nanowires from electrolytic sulfate baths (Fig.

3). The stoichiometry (verified via XPS characterization) of the nanowires could be tailored from Mn_2O_3 – Mn_3O_4 – MnO_2 by adjusting deposition potential and bath chemistry. Although the latter composition is most desirable for battery and supercapacitor applications, the other stoichiometries may be of interest for high surface area catalysis applications.

C. SIGNIFICANCE OF RESULTS

We have been able to successfully synthesize various transition metal oxide cathodes, e.g., cobalt and nickel oxides, in the form of nanowires with typical diameters of 20nm. In addition, arrays of free-standing manganese oxide nanowires with comparable electrochemical activity have been synthesized. Combining such nanowire cathodes with a lithium anode in a suitable device, i.e., either with a polymer electrolyte cast from solution, or solid electrolyte, sputter or vapor deposited, will result in a thin film battery with a several-fold increase in the power densities, which is one deterrent factor for polymer electrolyte, or thin film or microbatteries.

D. FINANCIAL STATUS

The total funding for this task was $115,000, of which about $30,000 was spent for in-house efforts and $25,000 was transferred to the collaborator, Caltech.

E. PERSONNEL

No other personnel were involved.

F. PUBLICATIONS

1) W. C. West, N. V. Myung, J. F. Whitacre, and B. V. Ratnakumar, "Synthesis of LiCoO2 Nanowire Arrays from Co Electrodeposits," presented at the Nanophase Materials for Batteries and Fuel Cells Symposium at the American Electrochemical Society Spring Meeting, Philadelphia, May 2002.
2) W. C. West, N. Myung, J. Whitacre, B. V. Ratnakumar, "Direct Electrolytic Deposition of Manganese Oxide Nanowires for High Power Battery and Capacitor Electrodes," an NTR describing processes to fabricate nanostructured electrode materials from templated nanowires, *NASA Novel Technology Report # 30655*, (2002).
3) The group was solicited to present an invited paper describing nanostructured materials for batteries at the NanoEnergy Conference in Miami, FL in Dec. 2002. Will West will present "Freestanding Arrays of Nanowire Materials for High Rate Capability Battery Electrodes."

G. REFERENCES

1) N. Li, C. R. Martin, and B. Scrosati, *Electrochem. and Solid State Lett.,* **3** 316 (2000).

2) For example: F. Croce, C. Sides, B. Scrosati, and C. R. Martin, abstract 172, *May 2002 Meeting of the Electrochemical Society*.

H. FIGURES

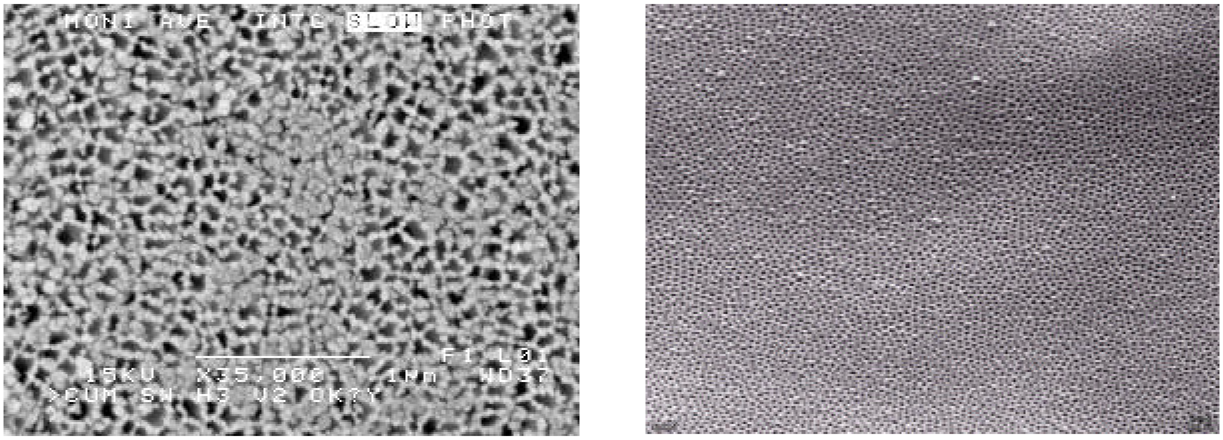

Fig. 1 Whatman Anodisc (100 nm pores) JPL synthesized alumina template (20 nm pores)

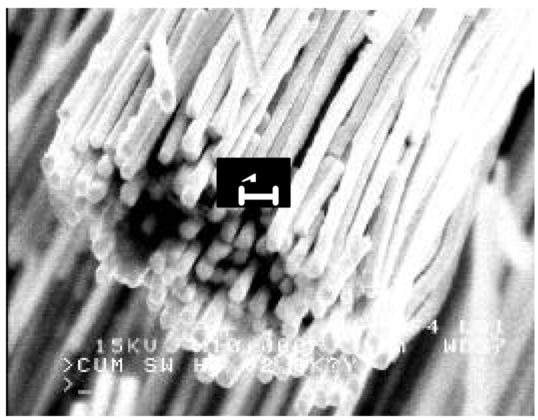

Fig.2. Nanowires of Co(Ni) for fabrication of nanostructured $LiCoO_2$.

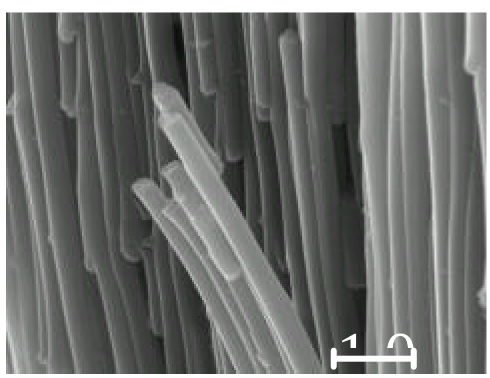

Fig.3. Nanowires of Manganese oxides from sulfate bath